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Photosolvolysis of 3,4-Dichloroaniline in Water Evidence for an Aryl Cation Intermediate

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16. ABSTRACT

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PHOTOSOLVOLYSIS OF 3,4-DICHLOROANILINE IN WATER
EVIDENCE FOR AN ARYL CATION INTERMEDIATE

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Abstract—Irradiation of 3,4-dichloroaniline in water ($\lambda > 290$ nm) gave 2-chloro-5-aminophenol with a conversion of $78 \pm 5\%$. The photolysis quantum yield at 313 nm of 0.052 ± 0.003 was unaffected by cyanide (0.35 M) or pH changes between 4 and 12. A MO calculation indicated a large excited singlet state shift in electron density to the carbon undergoing substitution. The reaction is suggested to proceed through an aryl cation intermediate produced by heterolytic cleavage of the *meta* carbon–chlorine bond. Reaction from the triplet state is not considered likely since neither oxygen nor sorbic alcohol affected the quantum yield.

Aromatic photonucleophilic substitutions are known to be particularly facile processes for compounds with halogens *meta* to OH, NH_2 or OMe groups.[1–5] In water, for example, the *meta* chlorine of pentachlorophenol is preferentially replaced by OH.[5] These substitutions are generally observed to be solvolysis processes. Unless present at extremely high concentrations, specific added nucleophiles are ineffective in competing with the solvent for replacing the halogen. For example, even 0.35 M aqueous cyanide, an excellent nucleophile, was ineffective in trapping electronically excited 3-chlorophenol; resorcinol accounted for 65–72% of the loss of starting material.[2] The authors suggest that either the excited state or the reactive species derived therefrom is so reactive towards nucleophilic attack that it reacts faster with water than the other available nucleophiles.

During an investigation of the environmental fate of 3,4-dichloroaniline (DCA), the main photoproduct was found to be 2-chloro-5-aminophenol when irradiated ($\lambda >$ 290 nm) in water at pH 5–7. Conversion of $78 \pm 5\%$ was a lower limit because 2-chloro-5-aminophenol degraded three times more rapidly than DCA in a separate photolysis experiment under identical aerated conditions. A minor amount (2%) of 3- chloroaniline was also produced. Irradiation of DCA in deionized water also resulted in a lowering of the pH of the solution. A second order reaction with hydroxide appeared unlikely because of the low hydroxide concentration.

More detailed kinetic studies (Table 1) in buffered solutions between pH 4 and 10 clearly demonstrated an insensitivity of the disappearance quantum yield to variations in the hydroxide concentrations. Similarly, no difference in quantum efficiency was noted for loss of DCA in 0.1 M KCN–0.2 M K_2CO_3 solution compared with that of DCA in distilled water at pH 6. Because neither hydroxide nor cyanide affect the photolysis rate, a bimolecular nucleophilic (S_N2) mechanism is improbable.

Recent theoretical work by Epiotis and Shaik[6] additionally predicts that if an S_N2 process were involved, it would occur at the 4 carbon because "...a photochemical nucleophilic aromatic substitution will occur in a manner which involves attack of the site of the aromatic molecule having the HO (highest occupied) electron density and, simultaneously, the smallest LU (lowest unoccupied) electron density". Using the Parsier–Parr–Pople pi electron molecular orbital method, electron densities were calculated in the total pi system in the ground (S_0) and excited (S_1) states of DCA and also in the highest occupied and lowest unoccupied molecular orbitals (Table 2). Carbon 3, the reacting center, has the smallest carbon HO electron density and the largest LU carbon density. The situation on carbon 4 is reversed; that is, a larger HO electron density and a smaller LU electron density. Consequently, a *second order* nucleophilic reaction is predicted to occur on carbon 4 producing 2-chloro-4-aminophenol, a product not experimentally observed.

The excited state *ortho–meta* directing activity of electron-donating groups is well known.[7] The first excited singlet state of DCA corresponds to the promotion of one of the lone pair electrons on the nitrogen into the LU orbital. The net effect is a decrease of 0.36 electron (Table 2) on the nitrogen and a corresponding increase in the aromatic ring, primarily on the *ortho* and *meta* positions. Carbon 3 receives the largest increase in charge (0.20 electron). Although reaction from a triplet state cannot be rigorously excluded, the rate of photolysis was not affected by the presence of oxygen,[8] and only slightly by the presence of 0.1 M sorbic alcohol[9] (Table 1), both of which are efficient triplet state quenchers.

The absence of any effect of added nucleophiles on the rate, the relatively large electron density increase on carbon 3 in the first excited singlet state, and the hydroxylated photoproduct suggest that the reaction

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Table 1. Quantum yields for reaction of DCA at 313 nm[a,b,c]

Solvent	Quantum Yield
Water pH 4	0.053 ± .002[d]
Water pH 5.5	0.049 ± .002[d]
Water pH 6.0	0.053 ± .002[d]
	0.052 ± .005[e]
Water pH 10	0.053 ± .002[d]
Water 0.1 M KCN 0.2 M K_2CO_3	0.053 ± .002[d]
Water Degassed (pH 6.2)	0.054 ± .003[d,f]
Water 0.1 M Sorbic alcohol, degassed	0.048 ± .002[d,f]
Methanol	0.0046 ± .001[e]
Acetonitrile	< 0.0005[e]

[a]Medium pressure mercury arc filtered through 1 cm of aqueous 0.001 M potassium chromate - 3 percent potassium carbonate and 3 mm Pyrex glass.

[b]Benzophenone-pentadiene actinometer.

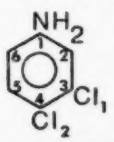
[c]The quantum yield in water was determined to be independent of light intensity.

[d]Calculated by the method of Zepp[16]; first order rate loss (absorbance in 1 cm pathlength <.01).

[e]>99 percent of the light absorbed.

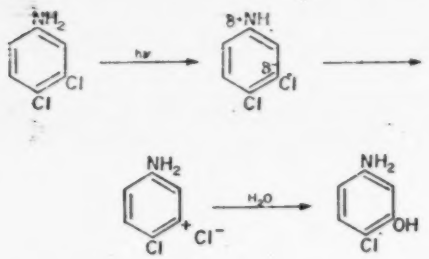
[f]Degassing was accomplished by three cycles of freezing and thawing under vacuum.

Table 2 DCA π electron densities



	Orbital densities		Total π densities		
Atom	Highest Occupied	Lowest Unoccupied	Ground State (S_o)	Excited State (S_1)	Charge Change
N	0.47	0.00	1.86	1.50	+.36
C_1	0.07	0.02	0.94	0.97	-.03
C_2	0.12	0.19	1.06	1.09	-.03
C_3	0.31	0.32	1.04	1.24	-.20
C_4	0.16	0.03	1.08	1.04	+.04
C_5	0.02	0.14	0.98	1.09	-.09
C_6	0.12	0.28	1.08	1.16	-.08
Cl_1	0.00	0.01	1.98	1.96	+.02
Cl_2	0.02	0.00	1.98	1.96	+.02

proceeds via an AS_NI mechanism involving an aryl cation intermediate (eqn 1).



(1)

The proposed mechanism is similar to that suggested by Cornelisse and Havinga[4] for the photosolvolysis of 2-halo-pyridines. The reaction in water may be viewed as an ionic dissociation, induced by the large electron density on carbon 3. The intermediate aryl cation reacts nearly indiscriminately with surrounding nucleophiles (generally water). Unless added nucleophiles exist at concentrations near that of the solvent, they cannot approach the cation rapidly enough to react.[10] This mechanism is also consistent with results reported for pentachlorophenol in water[5] and meta halogenated phenols in water and alcohol.[2,3] The reaction may, in fact, be general for aromatic compounds having a pi electron donating substituent and a good leaving group at the *meta* position.†

Kropp *et al.*[11] have demonstrated the photochemical formation of alkyl cations from alkyl iodides using trapping experiments with acetonitrile-water and methanol. Similar experiments were performed with DCA; however, neither the predicted anisole nor the amide photoproducts were detected by glc-mass spectrometry. The failure of the trapping experiments is attributed to a change in reaction mechanism in going from water to the less polar solvents, methanol and wet acetonitrile. A mechanistic change is indicated by the sharp drop in disappearance quantum efficiency in the organic solvents (Table 1). Moreover, the major product in methanol and acetonitrile is 3-chloroaniline, a compound that probably forms via homolysis of the *para* carbon–chlorine bond. This reductive photodechlorination occurring at the *para* rather than *meta* carbon also indicates that the photoreaction in water does not proceed via carbon–chlorine homolysis at the 3-carbon followed by electron transfer to form the aryl cation. Such a mechanism accounts for the photosolvolysis of alkyl iodides in polar hydroxylic solvents.[11]

The preferential photoreduction of *para* relative to *meta* halogens in aromatic compounds having electron releasing groups have been previously demonstrated.[12–14] For instance, while the major photoproduct of pentachlorophenol in water is tetrachlororesorcinol,[5] in hexane photoreduction to 2,3,5,6-tetrachlorophenol is predominent.[14] Photoreduction is suggested to proceed following bond homolysis from either a π^* or a σ^* triplet state, or, alternatively by electron transfer from a suitable donor.[13,15–18] The reason for preferential *para* photoreduction is, however, unclear.

EXPERIMENTAL

3,4-Dichloroaniline (DCA), obtained from Aldrich Chemical Company, was recrystallized three times from 95% EtOH (m.p. 72°). 2-Chloro-5-aminophenol was synthesized by the procedure of Moilanen and Crosby,[19] m.p. 158–158.5 (lit.[21] 158°); mass spec: 143, 141, 106, 78, 51; IR (KBr): 3380, 3350 (NH), 1600, 1490 (Ph), 1520 (NH), 1390, 1210 (phenol). 3-Chloroaniline and 4-chloroaniline (Aldrich) were used without further purification.

Photochemical rate studies were performed in an apparatus previously described.[21] Monochromatic radiation (313 nm) was isolated from a Hanovia medium pressure mercury arc by filtering through 1 cm of aqueous 0.001 M potassium chromate–3% potassium carbonate and 3 mm Pyrex glass. Quantum yields were determined both by use of concentrated DCA solns absorbing greater than 99% of the 313 nm radiation and also by the first order method of Zepp[22] using 1 cm pathlength cells. In all first order experiments, concentrations of DCA (5×10^{-6} M) were sufficiently low that the absorbance of the irradiated solns was less than 0.01. Light intensity was determined using the benzophenone-*cis*-pentadiene actinometer.[23] DCA was extracted from the photolysis solns with benzene and quantitated on a Tracor 220 gas chromatograph equipped with a linearized ^{63}Ni electron capture detector.

Product studies were conducted by irradiating solns (200 ml) of DCA with Westinghouse FS40 sun lamps. The irradiated solns were extracted with three 200-ml volumes of CH_2Cl_2. Following concentration, the photoproduct and DCA were quantitated by flame ionization glc. 3-Chloroaniline and 4-chloroaniline were separated by high pressure liquid chromatography (hplc) on a reverse phase ODS column using 5% MeOH–water as the mobile phase. Photo-products in MeOH and 1% water in acetonitrile were identified by comparison of their mass spectra and glc and hplc retention times with those of authentic samples. Mass spectra were obtained on a Varian MAT 44 combined glc-mass spectrometer. Limited mass range scans failed to reveal the presence of 2-chloro-5-aminoanisole in methanol or 2-chloro-5-amino-acetamide in the wet acetonitrile.

Electron densities were calculated using the Parsier–Parr–Pople method with charge iteration developed by Grabe and Skancke[24] to take into account polarization of sigma core electrons and parameterization by Roos and Skancke,[25] Hojer[26] and Grabe.[27] The orbital densities (Table 2) were obtained by squaring the coefficients of the highest occupied and lowest unoccupied (virtual) orbitals.

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†An alternative mechanism suggested by the referee is:

$$ArCl \xrightarrow{h\nu} ArCl^* \longrightarrow Ar^+ + Cl^- \xrightarrow{H_2O} ArOH.$$

Although this mechanism cannot be ruled out by our experimental data, it appears unlikely since it offers no rational for the photoproduct distribution. Additionally, at 313 nm, excitation of DCA occurs from the highest occupied molecular orbital, which is primarily centered on the nitrogen. At pH 7.0 electron ejection from anilines is known to predominently produce anilino radicals,[28] which would not be expected to further eliminate chlorine.

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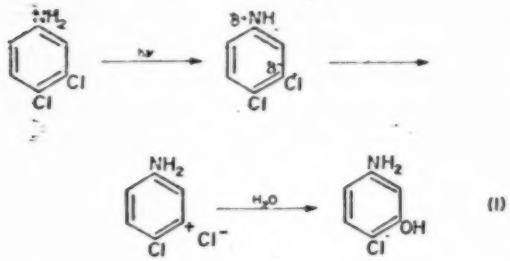

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